

# X-Ray Absorption Spectroscopy of Volatile Liquids and Their Surfaces



The Saykally Group

# X-Ray Spectroscopy of Liquid Microjets

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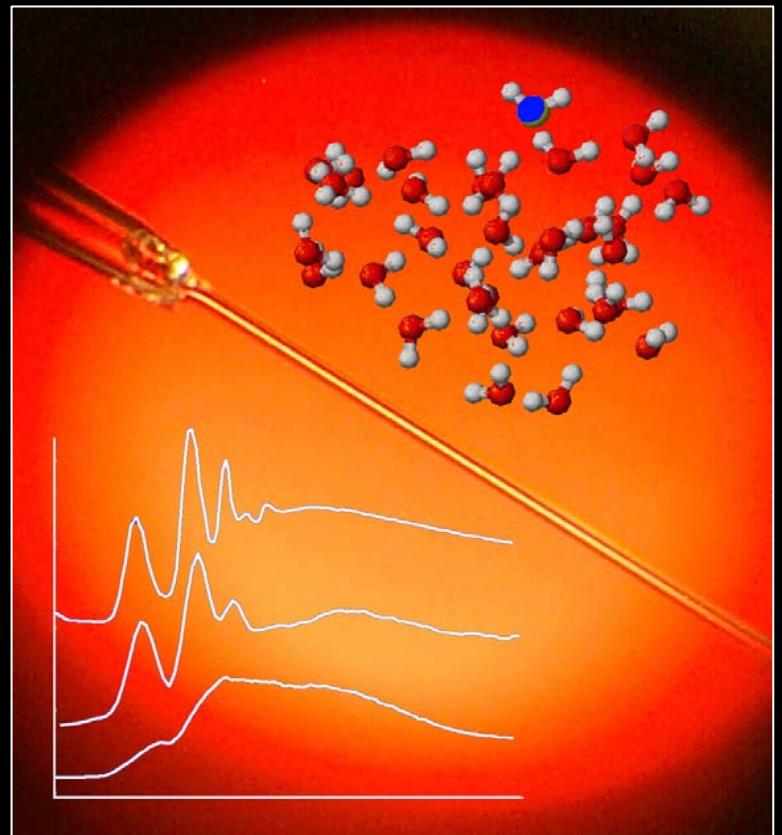
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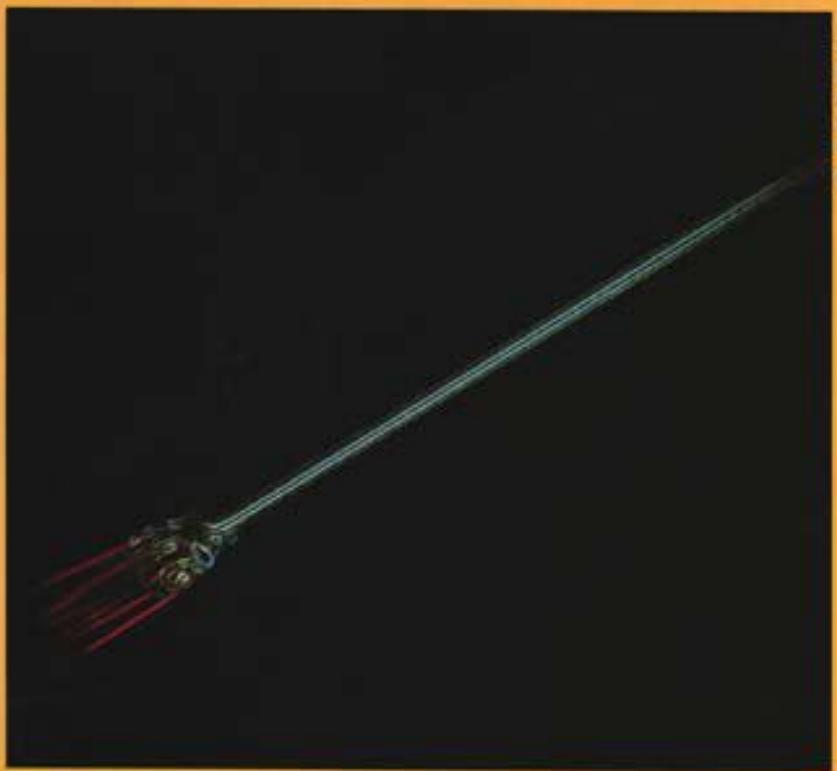
Matteo Cavalleri, Stockholm

Dr. Jim Tobin, LLNL



VOLUME 105  
MAY 3, 2001  
NUMBER 17  
<http://pubs.acs.org/JPCB>

THE JOURNAL OF  
**PHYSICAL  
CHEMISTRY B**



X-ray  
Spectroscopy of  
Liquid Water  
Microjets Probes  
Water Surface  
Structures  
(see page 3346)

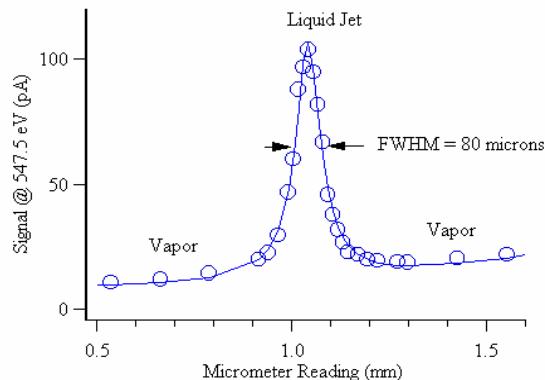
CONDENSED MATTER, MATERIALS, SURFACES, INTERFACES, & BIOPHYSICAL CHEMISTRY



# The Liquid Microjet Endstation:

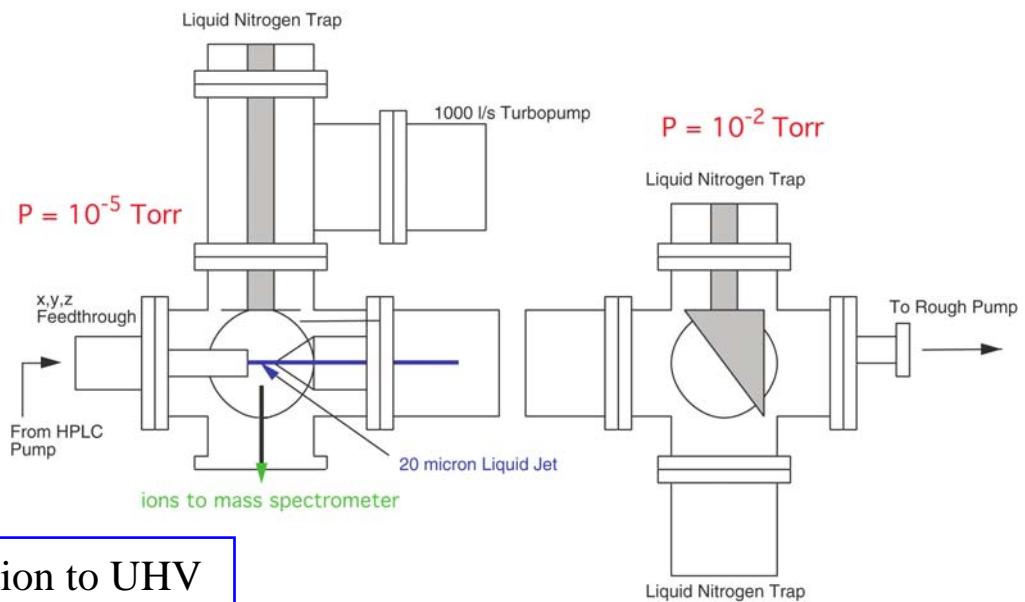
## Wilson et al, Rev Sci Inst. 2003

10-200X enhancement of liquid signals over vapor



Adiabatically pulled capillaries produce 1- 20 micron nozzles

High vacuum allows the analysis of electrons and ions emitted from volatile liquid surfaces



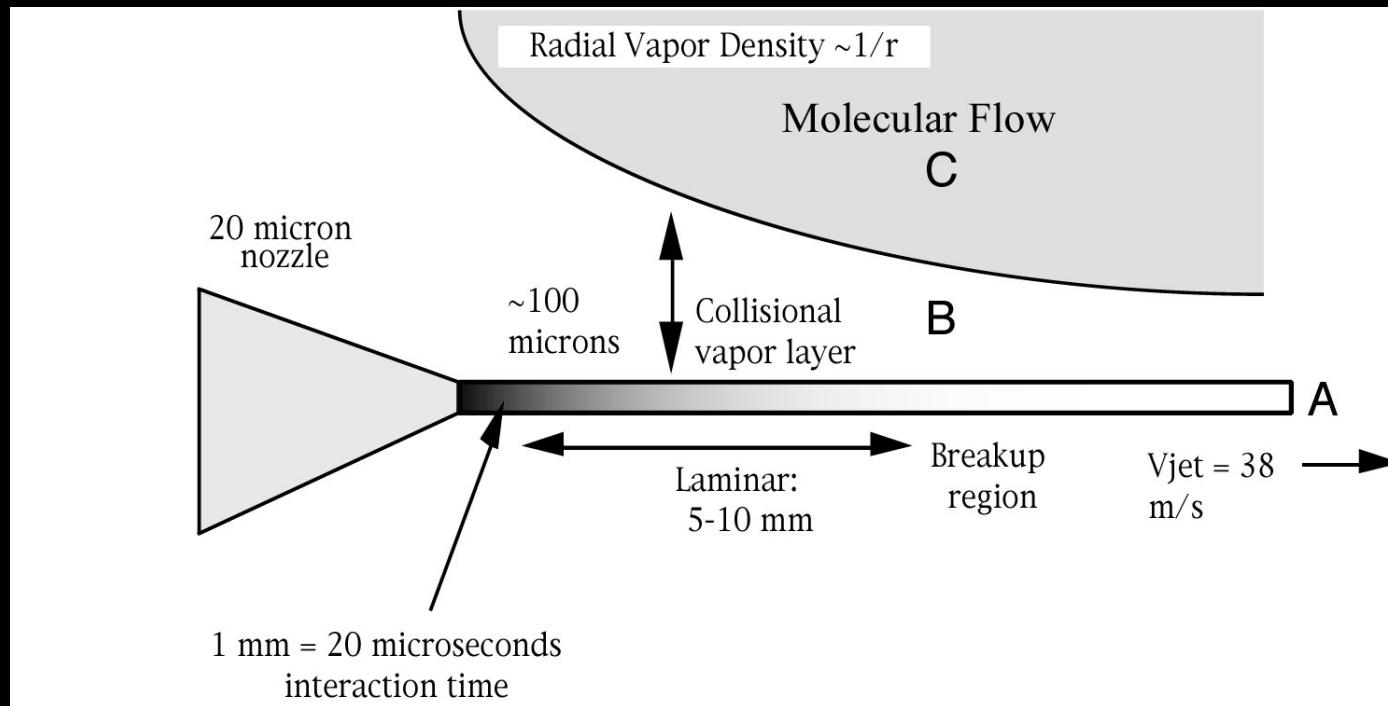
Windowless coupling of endstation to UHV environment of bl. 8.0

Not shown: three stages of differential pumping

# AN EQUILIBRIUM LIQUID-VAPOR INTERFACE

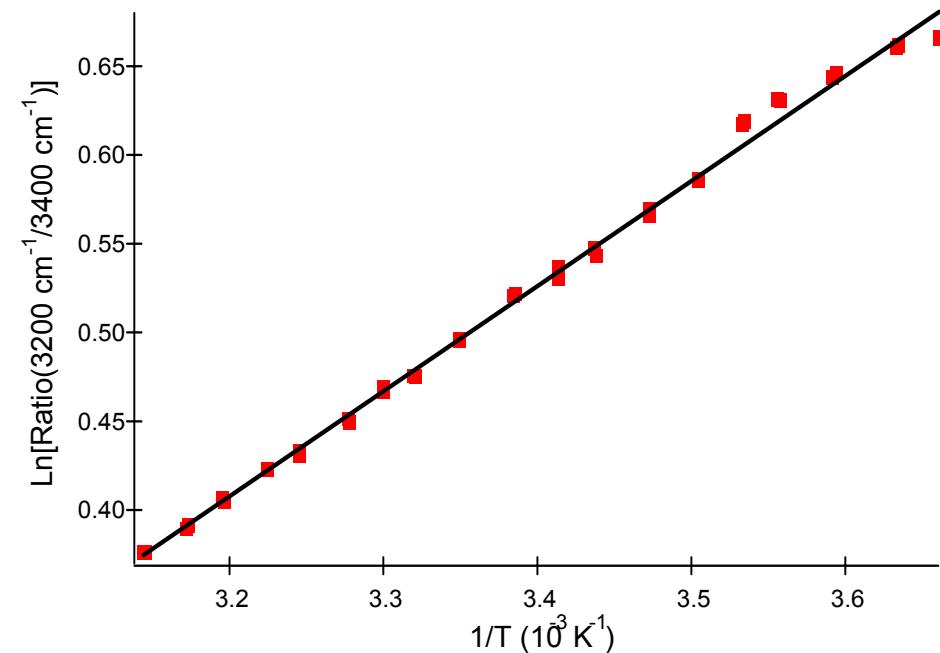
Wilson et al Rev Sci Inst 75, 725(2003)

## evaporation from a liquid microjet in vacuum



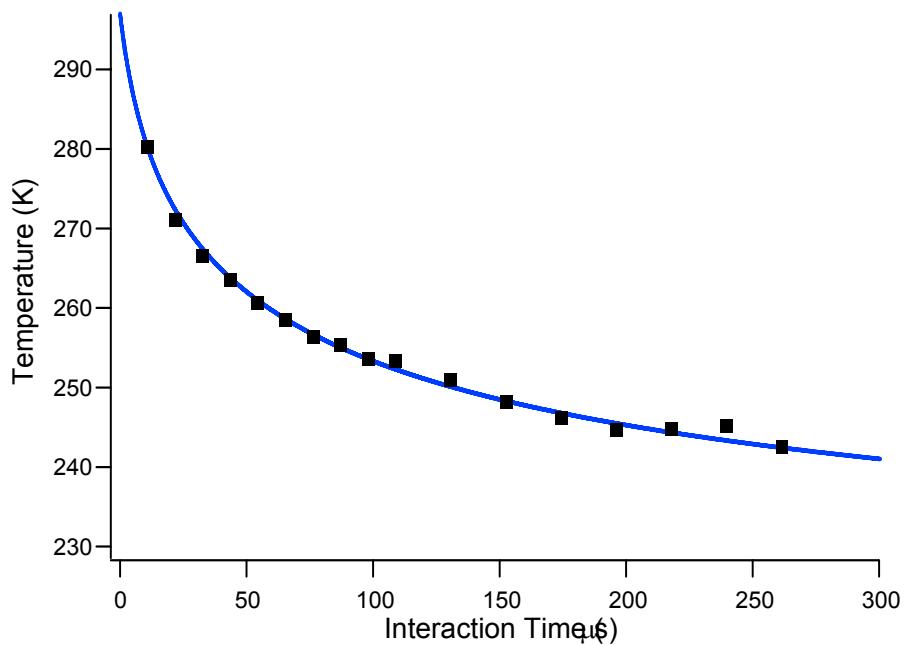
- Surface temperature sensitive to the vapor atmosphere surrounding the jet
- Thickness of vapor layer depends upon jet radius,  $r$ : (mean free path vs.  $r$ )

# Jet Temperature by Raman Spectroscopy



Ratio of band areas fit to  
Van't Hoff equation.

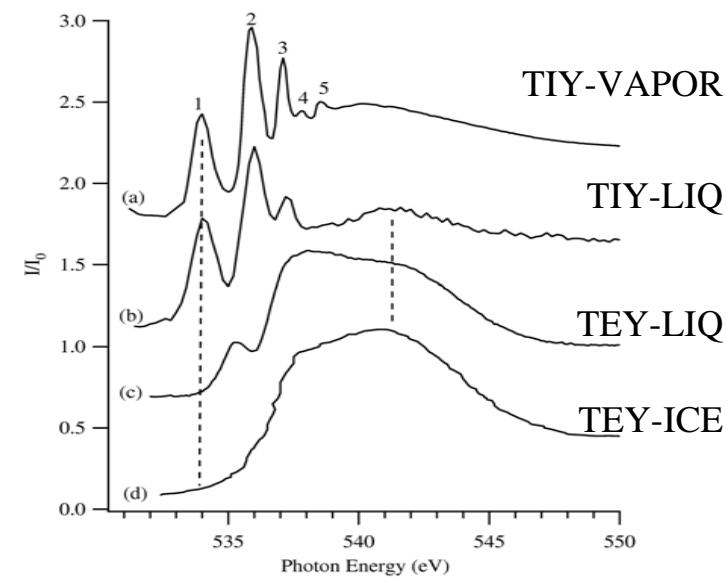
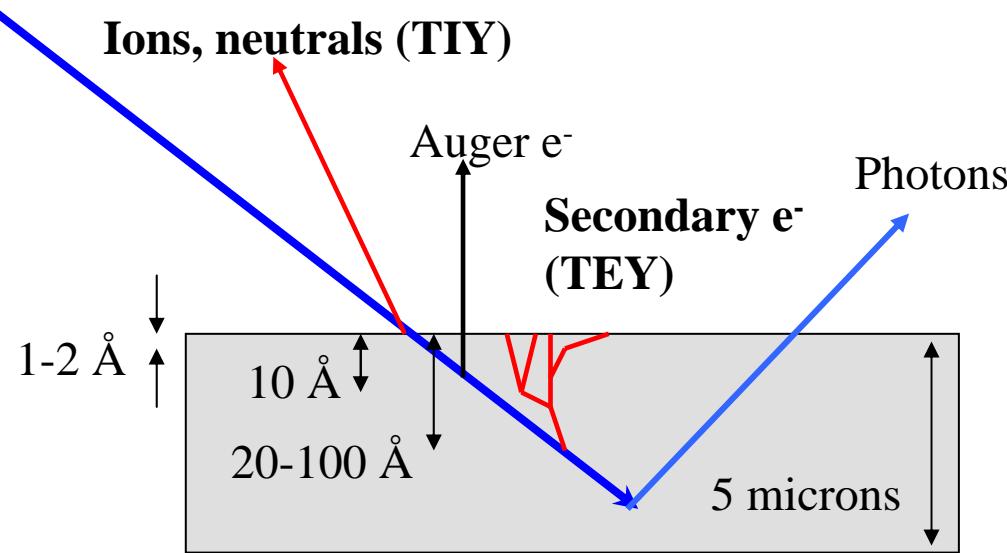
$$\frac{dT_o}{dt} = -\frac{\chi' 2}{r_o} \frac{n_e(T_o, P_o)}{\rho_l} \frac{\Delta H_{vap}}{C_p}$$



# Surface-Bulk Contrast in X-ray Absorption

Wilson et al, Rev Sci Inst. 2003

$$h\nu = 530 \text{ eV}$$



- Total Ion Yield (TIY)  $\sim$  surface
- Total Electron Yield (TEY)  $\sim$  bulk

# Beamline 8.0: Advanced Light Source



**Source characteristics:** 5-cm-period undulator (U5)

**Energy range:** 80-1400 eV (1.9 GeV)

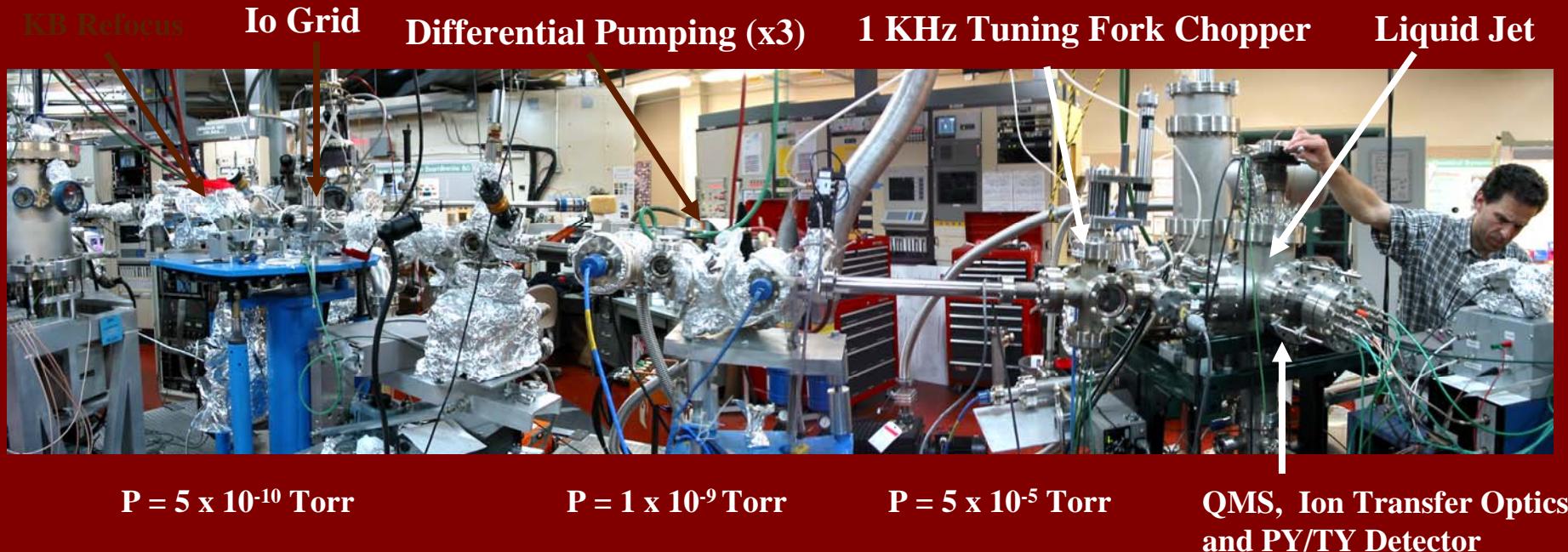
**Monochromator:** SGM (gratings: 150, 380, 925 lines/mm)

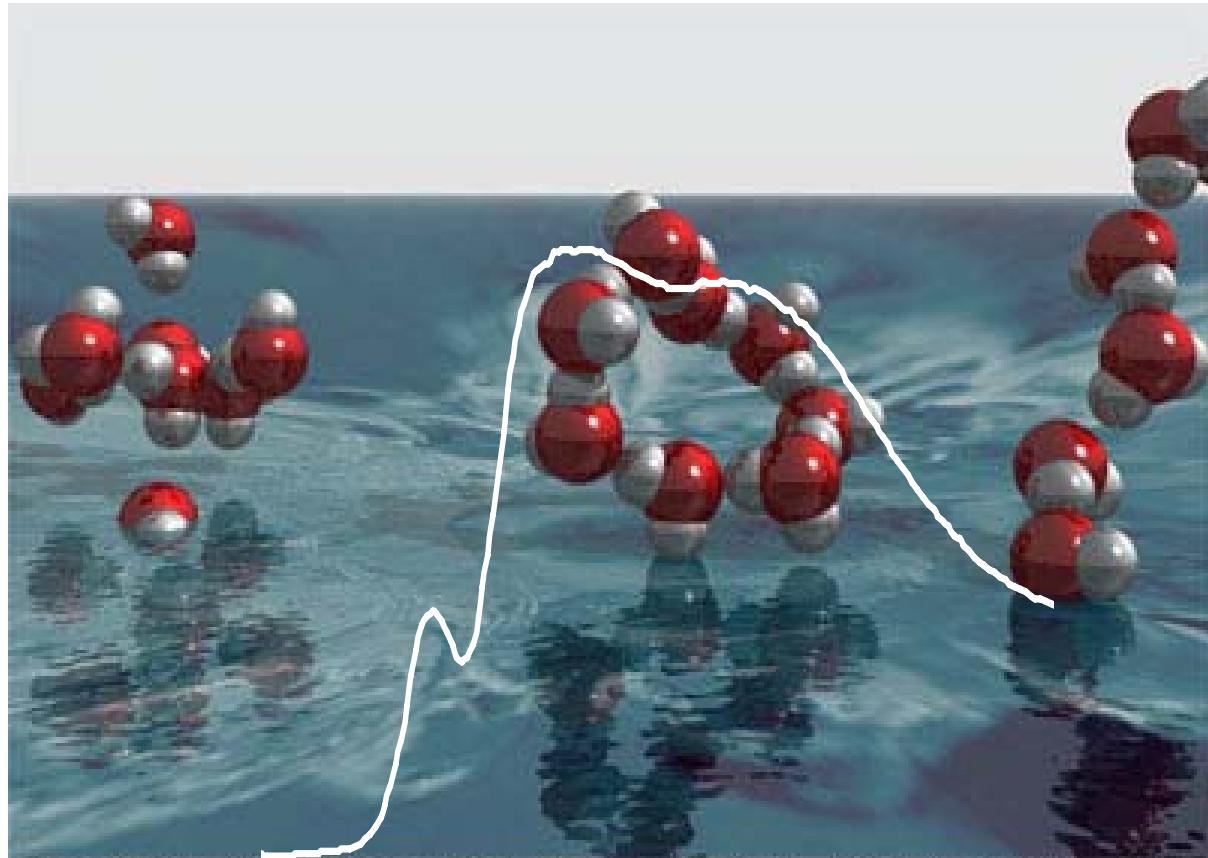
**Flux:**  $10^{11}$  to  $6 \times 10^{15}$  photons/s

**Resolving power:**  $(E/\Delta E) < 8000$

**Spot Size:** 80 x 100 microns (v x h)

# Microjet Endstation: Beamline 8.0





- Recent XRS/XAS results suggest water forms only 2 strong hydrogen bonds???
- Liquid water comprises primarily rings and chains???

Ph. Wernet et al., *Science*, **304** 995 (2004)

# Energetics of Hydrogen Bond Network Rearrangements in Supercooled Liquid Water

Smith,Cappa,Wilson,Cohen,Geissler,Messer,RJS

Science 306, 851(2004)

Science 308, 793(2005)

PNAS 102, 14171(2005)

# Effects of Salts on the Hydrogen Bond Network of Liquid Water

Cappa, Wilson, Messer, Gilles, Cohen, and RJS

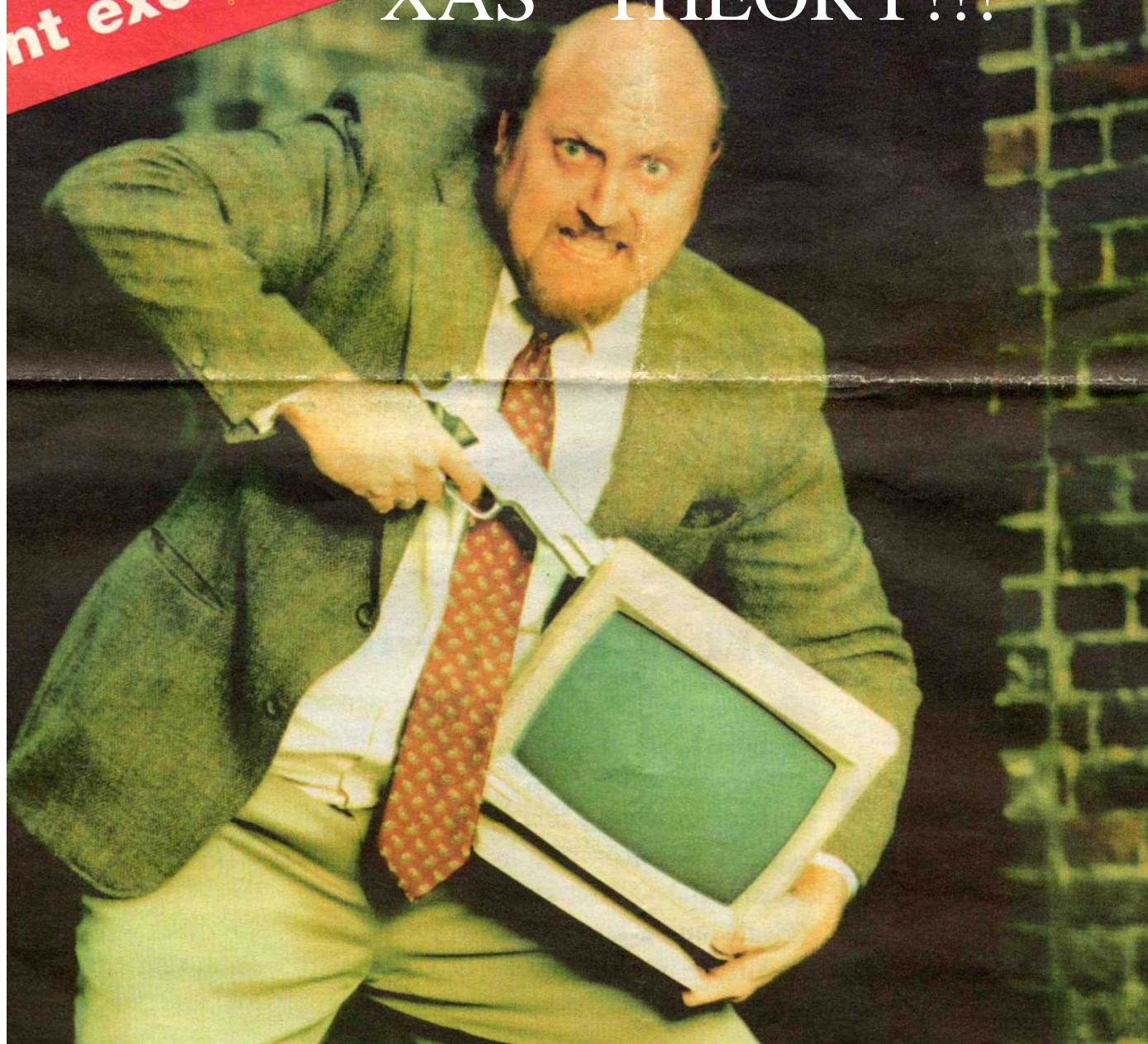
# ANIONS



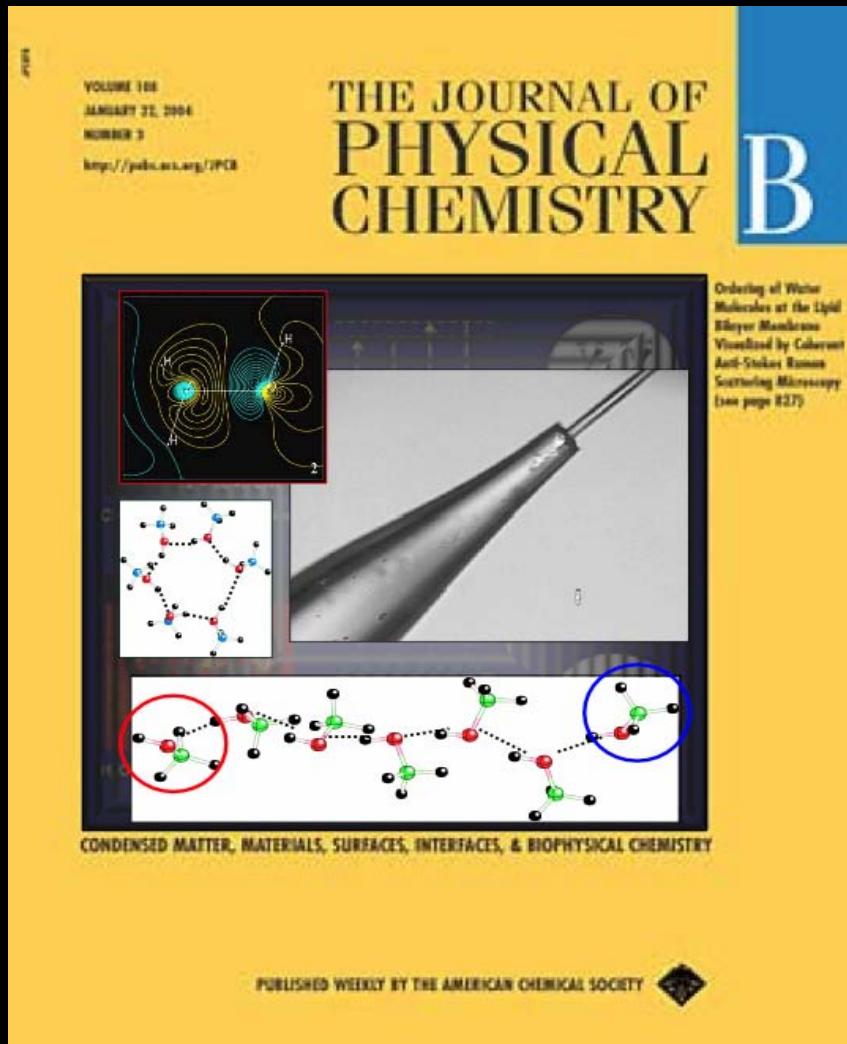
Cappa *et al.* *J. Phys. Chem. B*, 2005, 109, 7046

nt exclusif

# XAS THEORY!!!

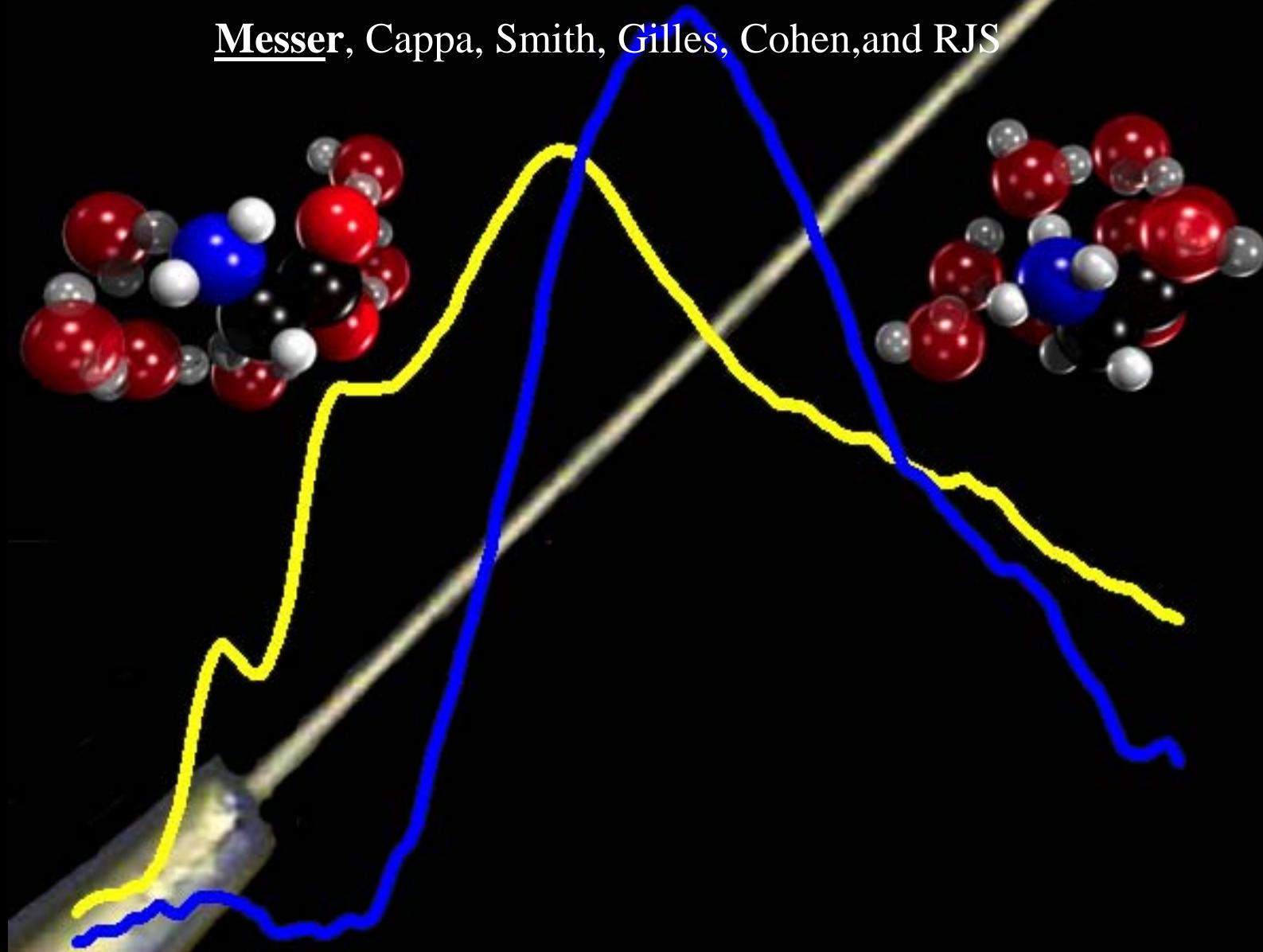


# X-Ray Spectroscopy of Liquid Methanol

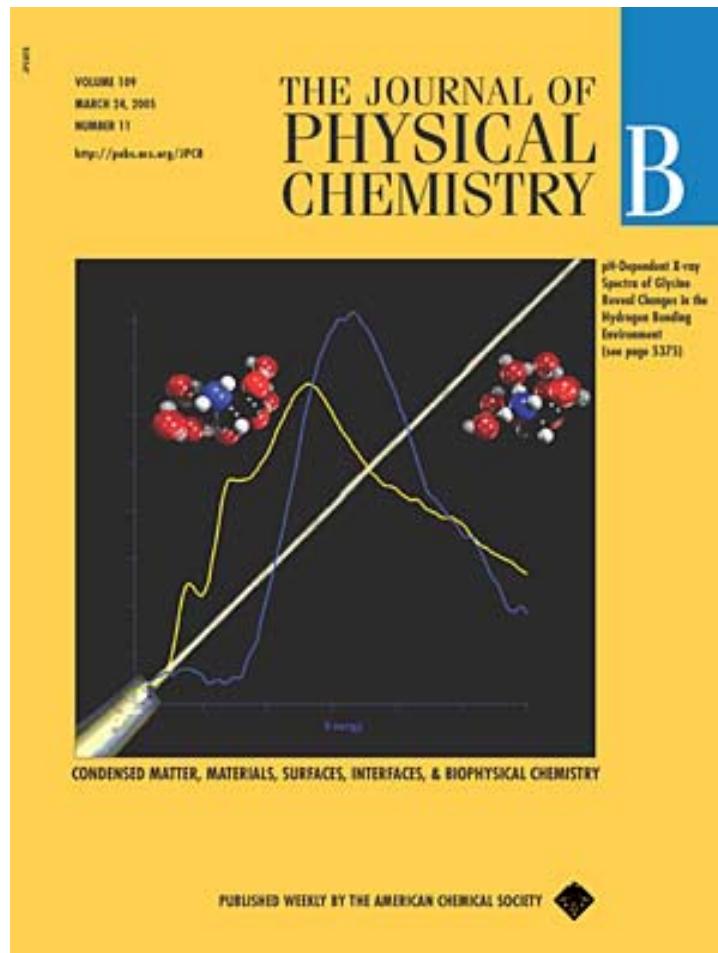


# pH dependence of the Electronic Structure of Amino Acids and Polypeptides

Messer, Cappa, Smith, Gilles, Cohen, and RJS



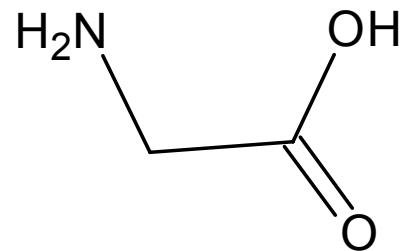
# pH Dependence of Glycine



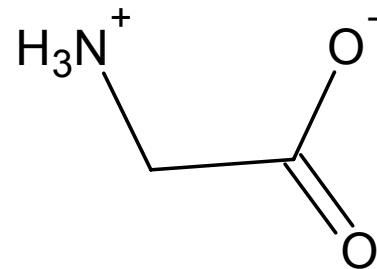
Messer, B. M.; Cappa, C. D.; Smith, J. D.; Wilson, K. R.; Gilles, M. K.; Cohen, R. C.; Saykally, R. J., *et al*, *Journal of Physical Chemistry B* **2005**, 109, (11), 5375

# Glycine

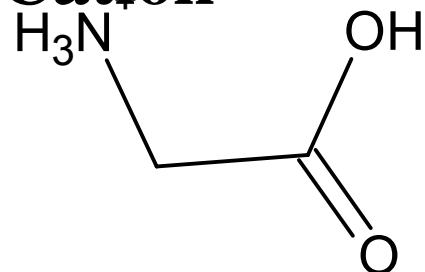
**Neutral**



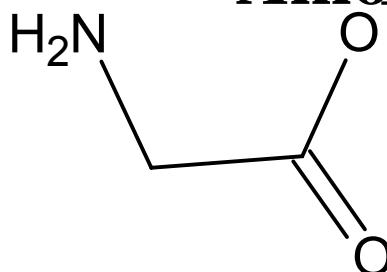
**Zwitterion**



**Cation**

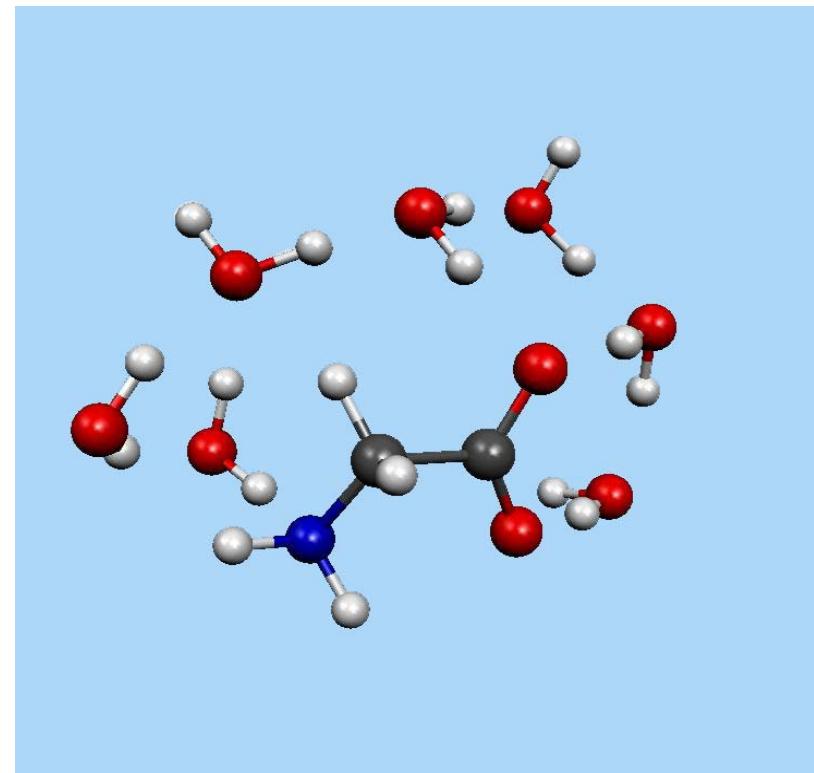


**Anion**

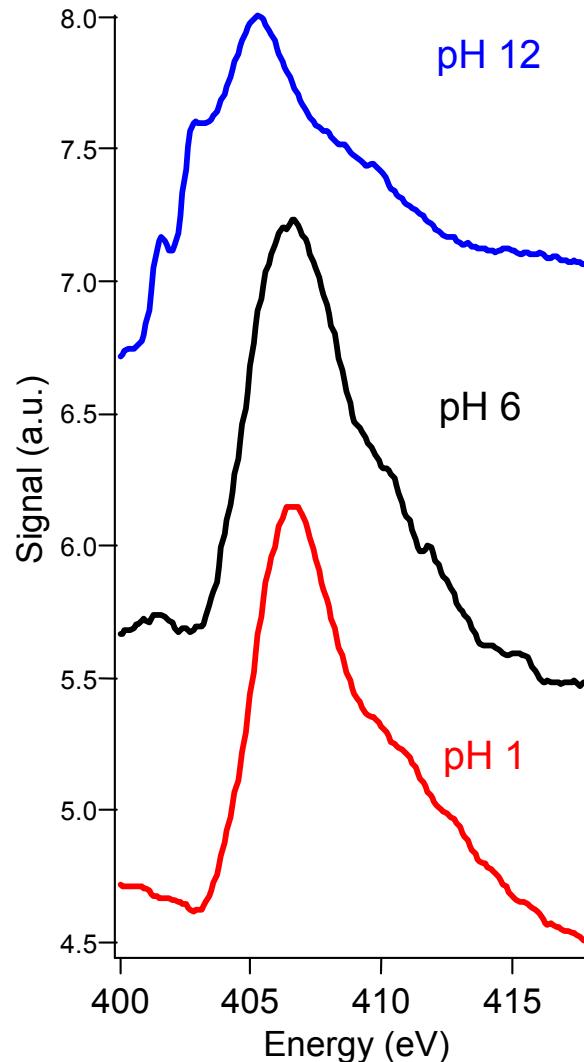
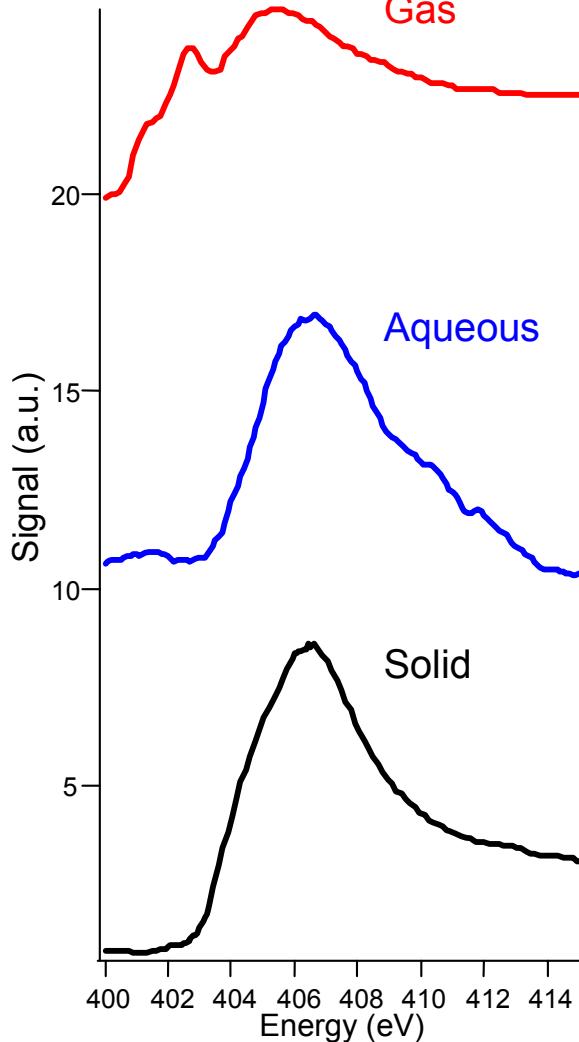


# Hydrated Clusters

- Created using Molecular Mechanics
- Optimized with DFT
- Provide test case for hydrated molecules
- Compare to isolated molecules to determine hydration effects

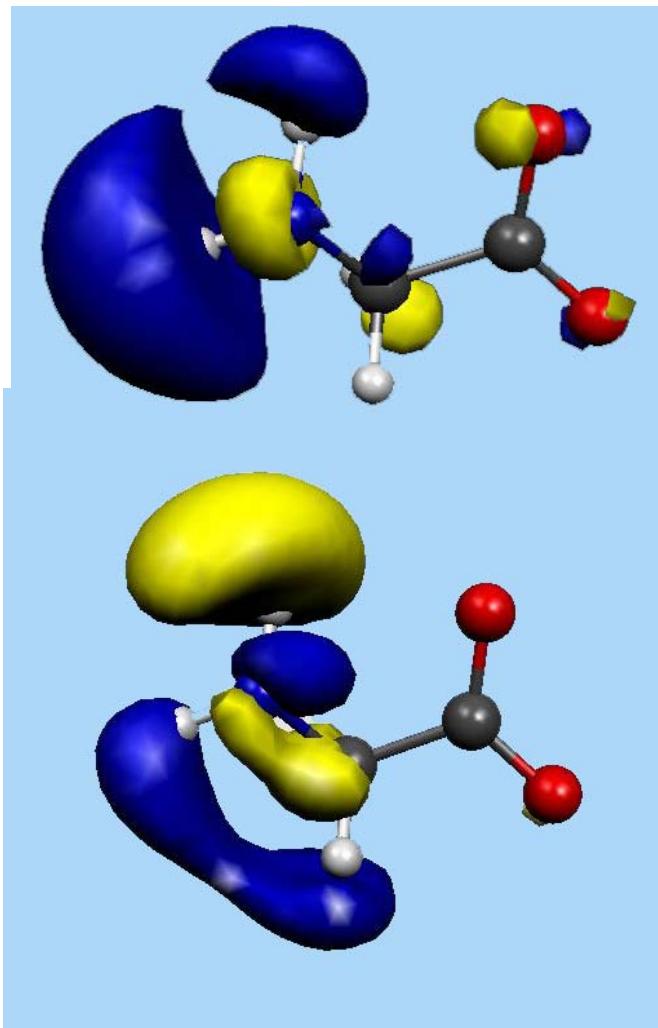


# Nitrogen K-edge



# Acceptor-Only Configuration

- Analogous to  $4a_1$  and  $2e$  orbitals of  $\text{NH}_3$
- Show strong H-bond dependence
- Not present in solid or on Cu(110)



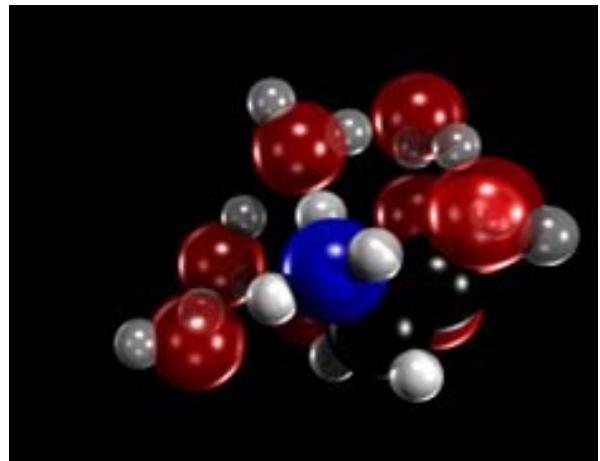
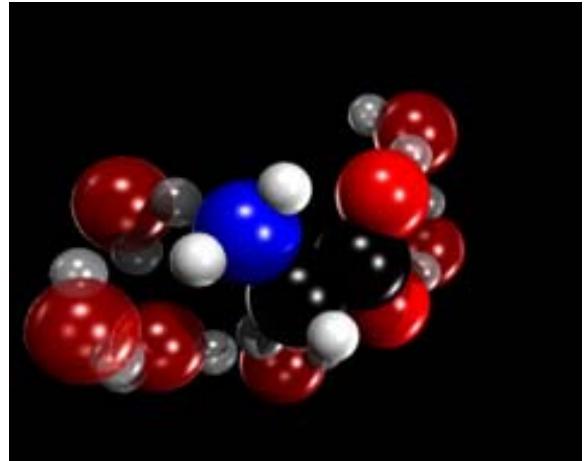
# Hydration of Amino Acids

When and how does “acceptor-only” occur?

Straight chain vs. cyclic amines

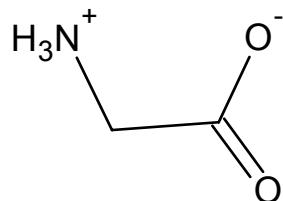
Amino acid vs. peptide

Buffer effects

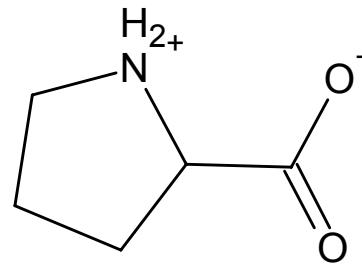


# Test Systems

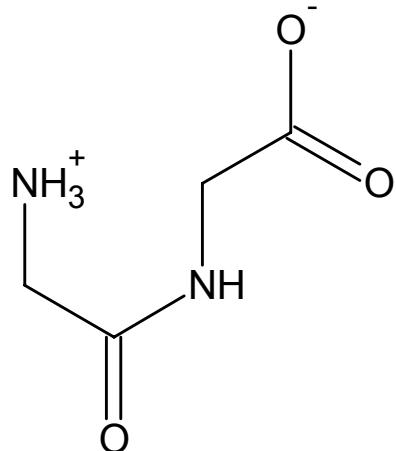
Gly



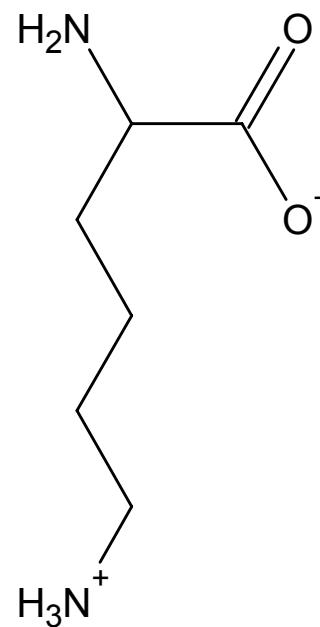
Pro



GlyGly

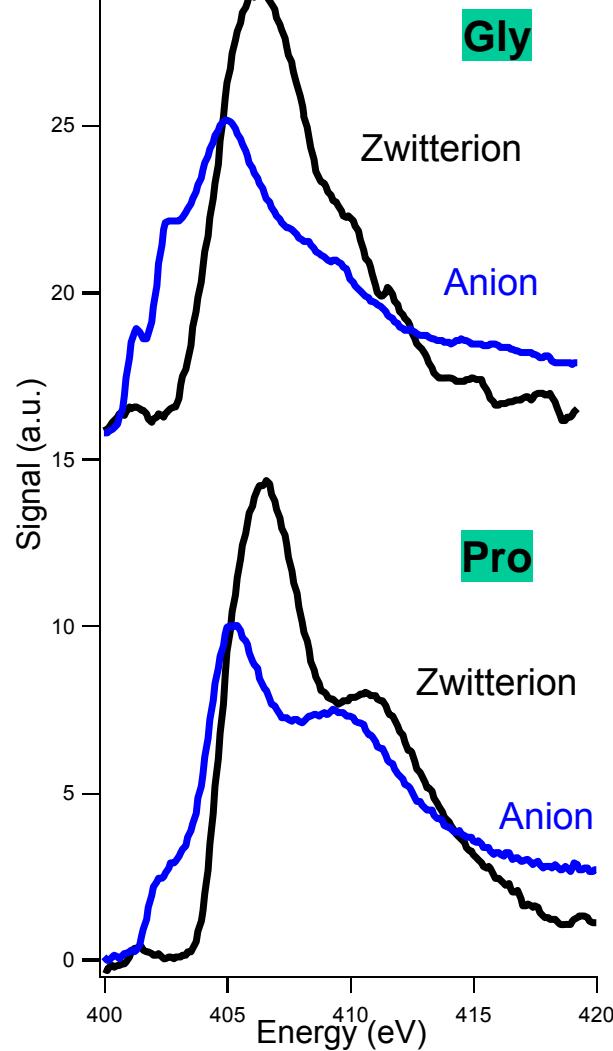


Lys



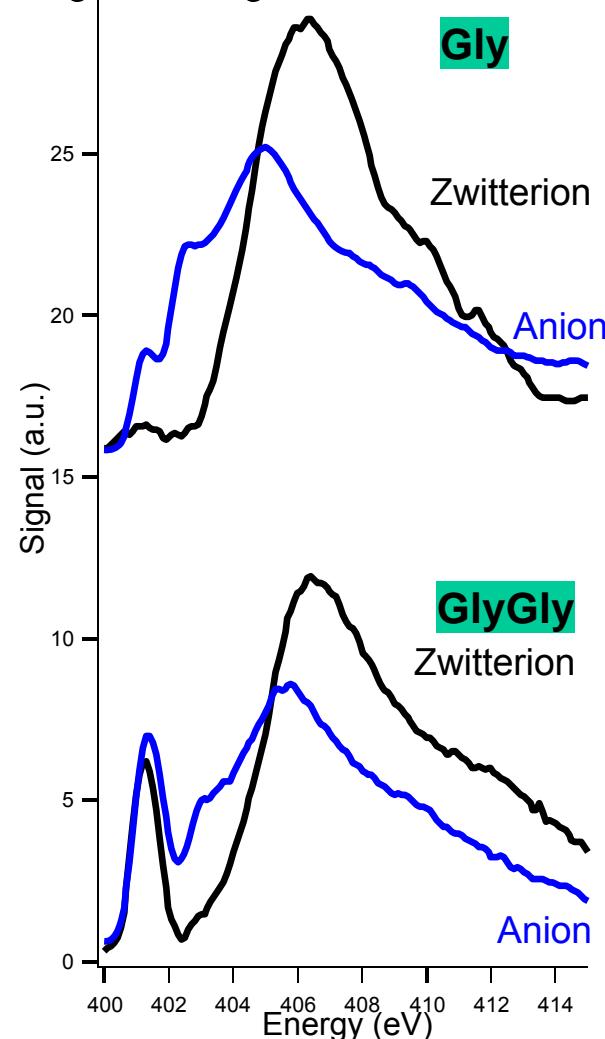
# Gly vs. Pro

- Similar red shift at high pH
- More pronounced post edge in Pro
- Pre-edge assigned to  $1s \rightarrow \sigma^*$  on side chain
- Acceptor-only not present



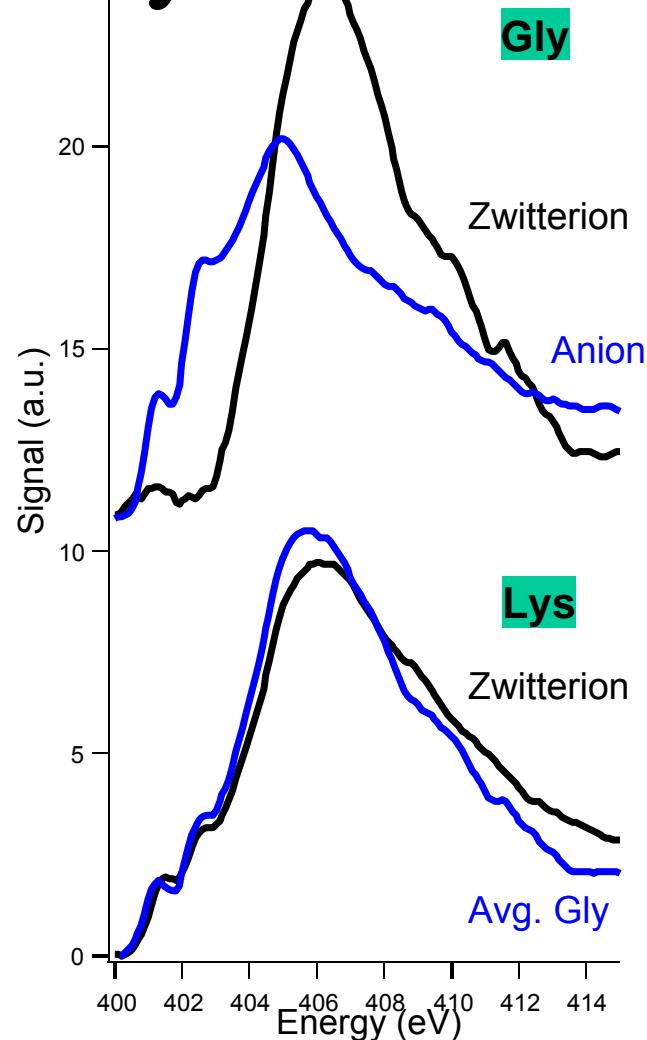
# Gly vs. GlyGly

- Broadened  $1s \rightarrow \pi^*$  at high pH
- Broad pre-edge resonance at high pH
- Acceptor-only present



# Gly vs. $^{25}\text{Lys}$

- Lys at pI (pH ~10)
- Resembles average of Gly spectra
- Lys  $\alpha$ -amine in acceptor only



# Conclusions

- First measurement of aqueous amino acid solutions...pH dependence
- Constantly renewed sample
- NEXAFS provides insight into local hydration environment

# Acknowledgements

Kevin Wilson

Mary Gilles

Bruce Rude

Tolek Tyliszczak

David Shuh

Jonathan Denlinger

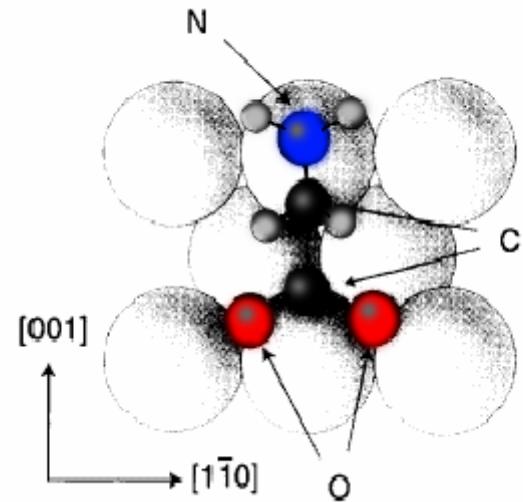
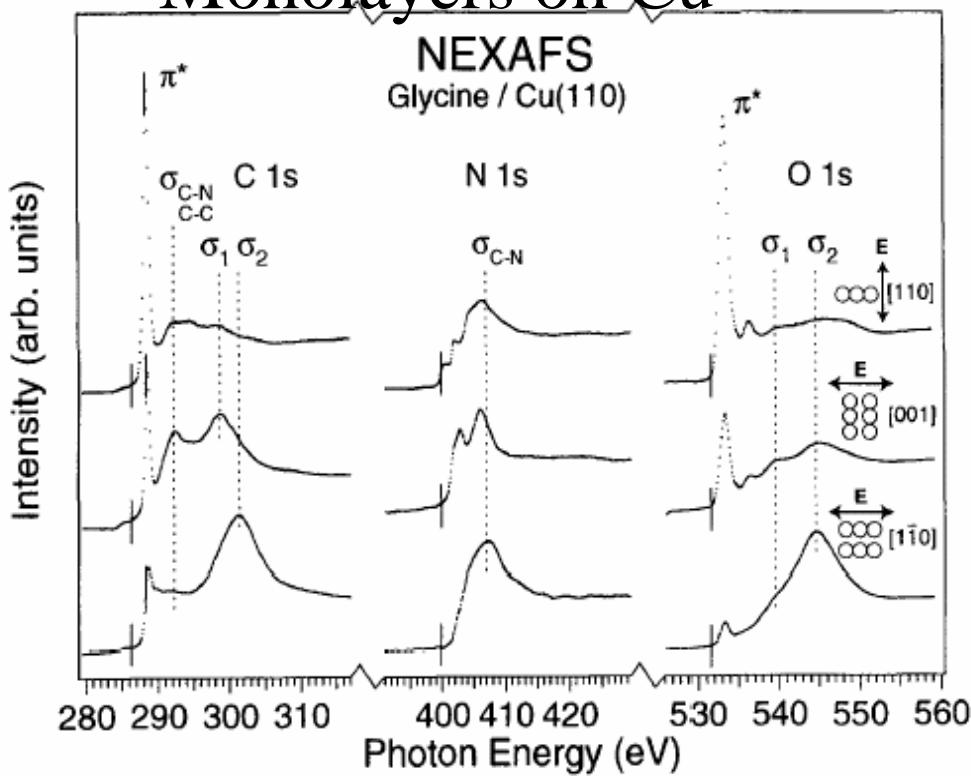
Klaus Hermann

# This talk is TERMINATED !!

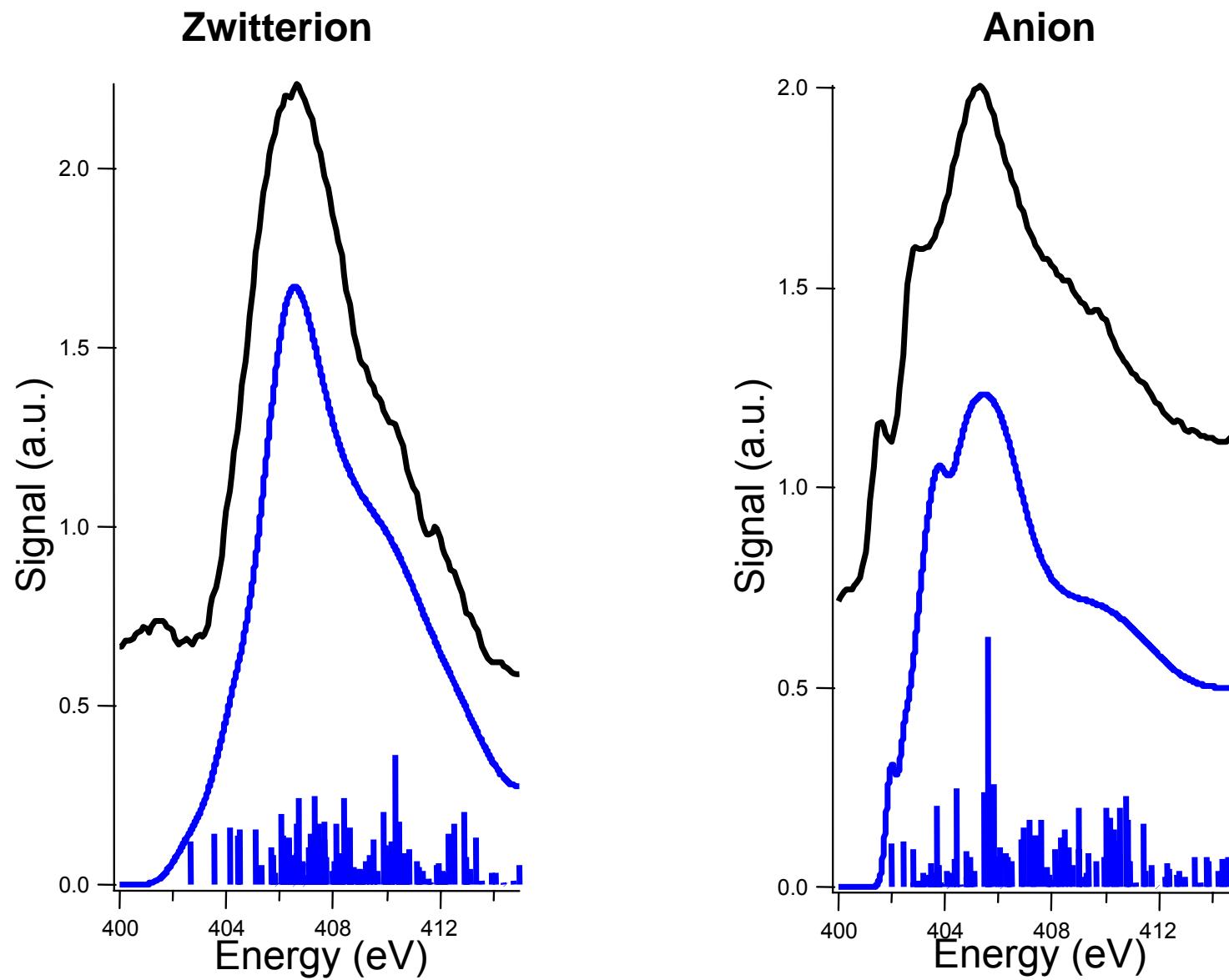


# XAS of Amino Acids

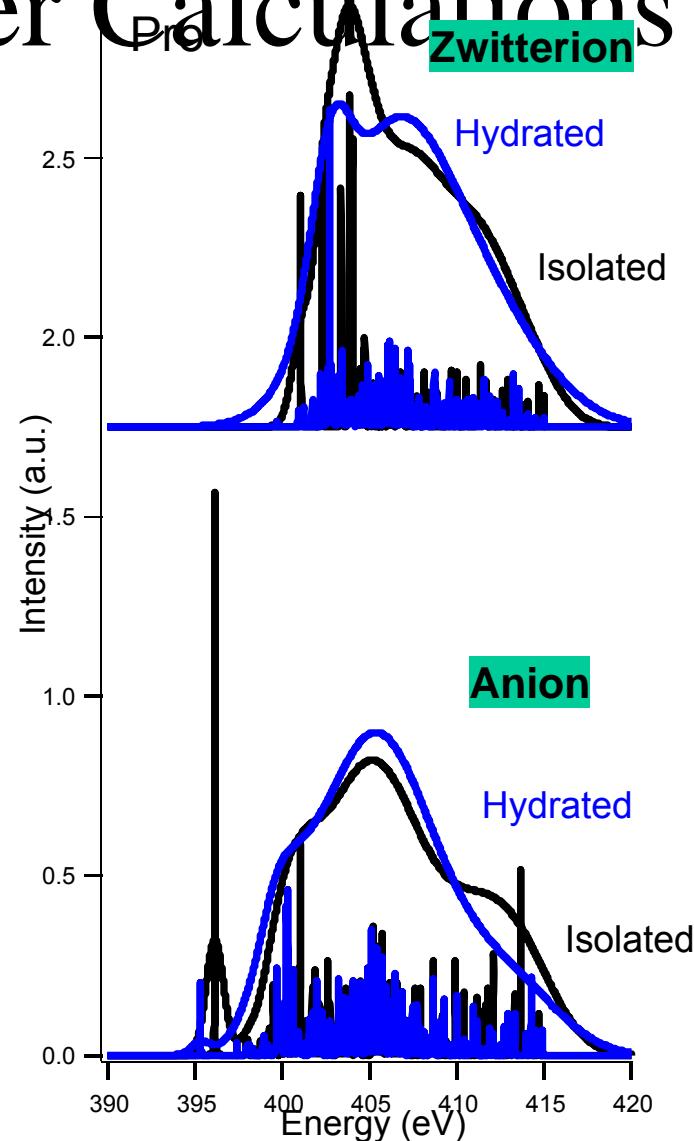
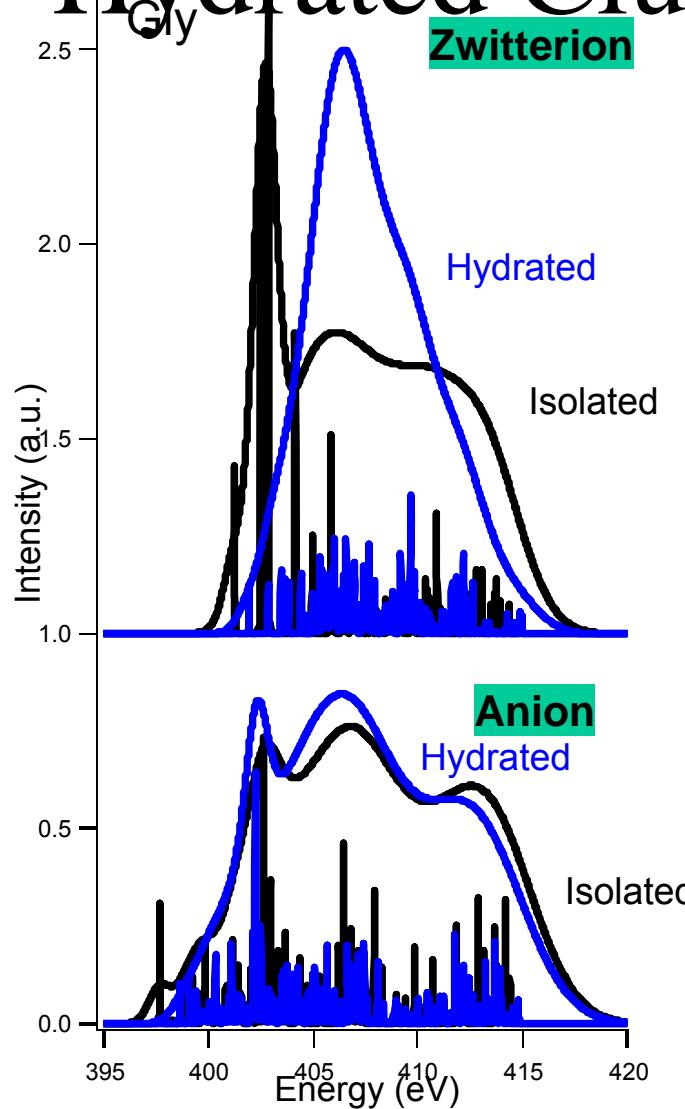
- Thin film samples
- Monolayers on Cu



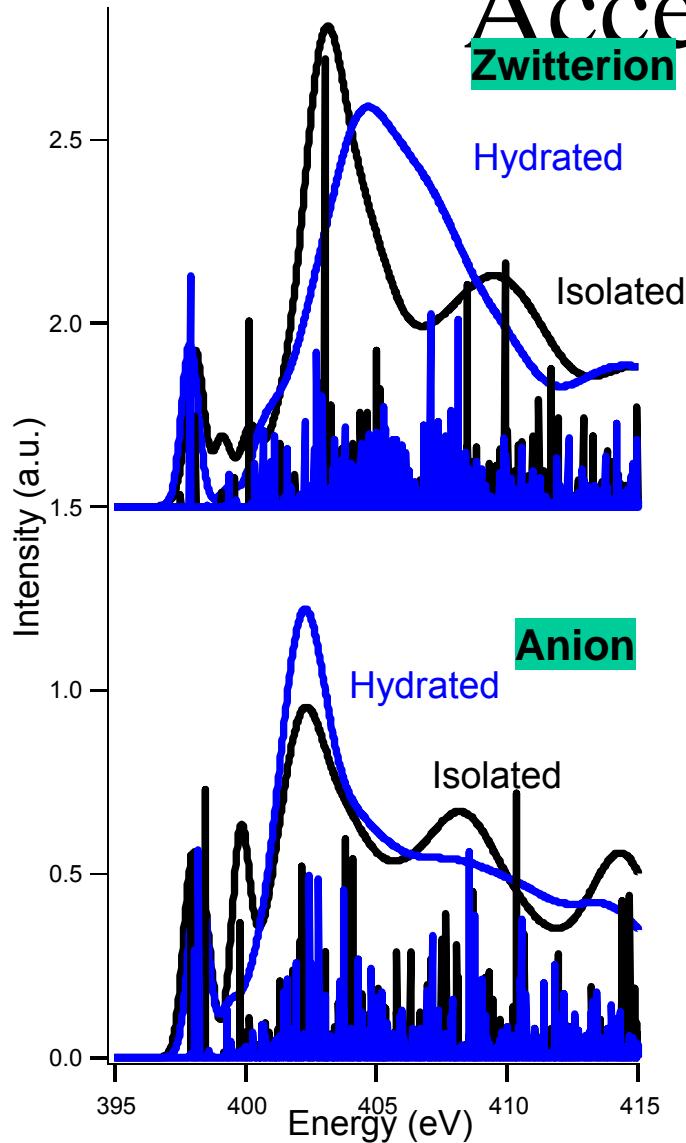
Kaznacheev, K et al *JPCA* **2002**, *106*, 3153.  
Gordon, M.L. et al *JPCA* **2003**, *107*, 6144.  
Hasselström, J. et al *Surf Sci* **1998**, *407*, 221.



# Hydrated Cluster Calculations

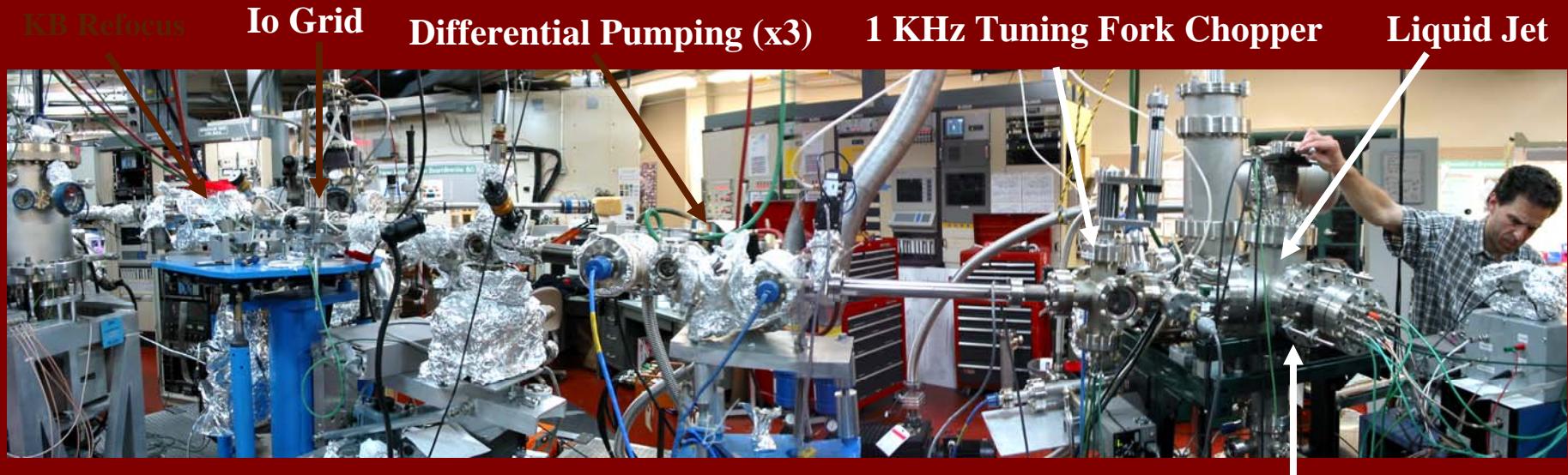


# Acceptor only ?



- $1s \rightarrow \sigma_{\text{NH}}^* \& \sigma_{\text{NH}_2}^*$  only transitions in region
- Significant broadening present

# Microjet Endstation: Beamline 8.0

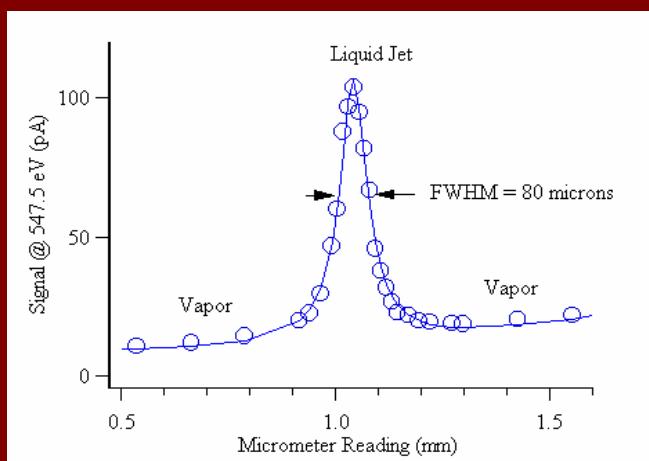


$P = 5 \times 10^{-10}$  Torr

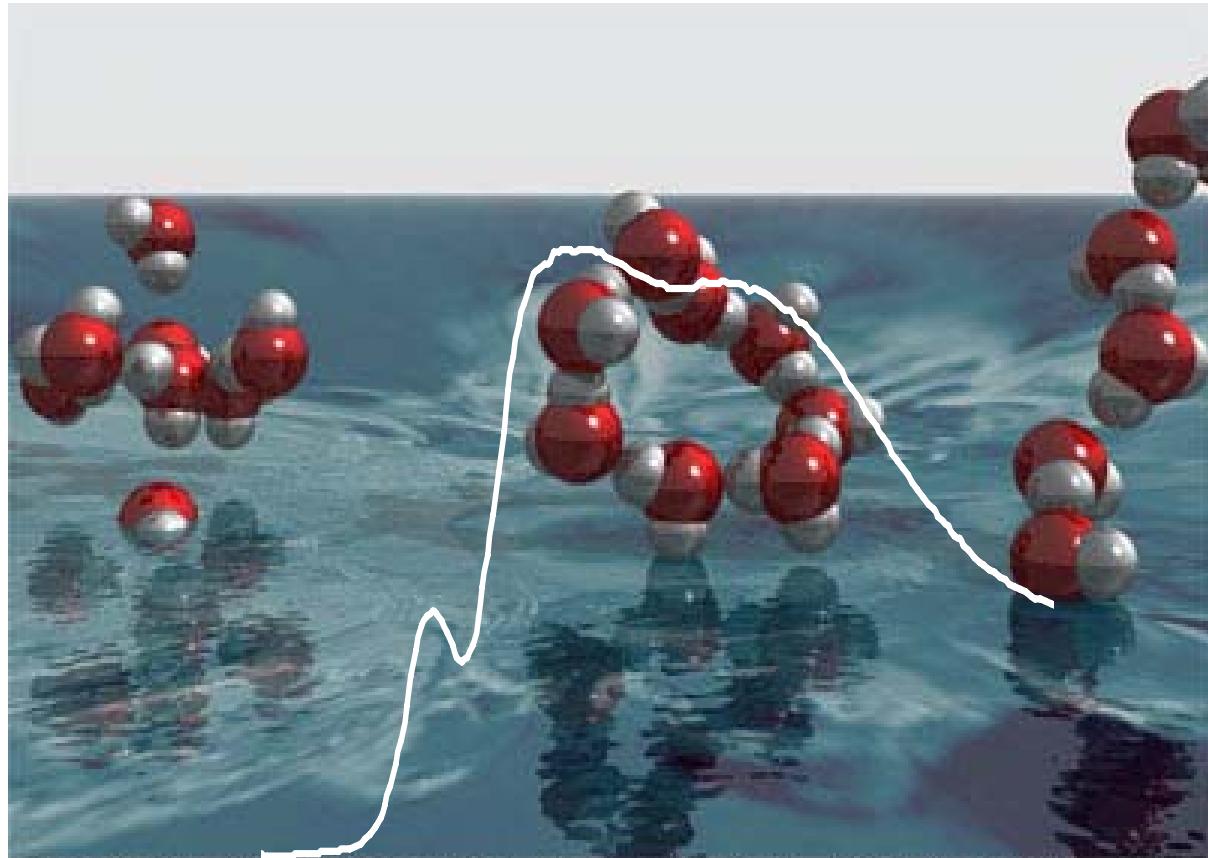
$P = 1 \times 10^{-9}$  Torr

$P = 5 \times 10^{-5}$  Torr

QMS, Ion Transfer Optics,  
and PY/TY Detector



10-20 X Enhancement of Liquid over  
Gas phase ion signals



- Recent XRS/XAS results suggest water forms only 2 strong hydrogen bonds???
- Liquid water comprises primarily rings and chains???

Ph. Wernet et al., *Science*, **304** 995 (2004)